

Dual Layer Coated High Porous SiC - A New Concept for SCR Integration into DPF

Thomas Wolff and Ramona Deinlein
Dinex GmbH

Henrik Christensen and Lars Larsen
Dinex A/S

ABSTRACT

The integration of DeNO_x functionality into wall flow filters for the after treatment of diesel engine exhaust gases is a field of technology to which many publications in the recent years have drawn their attention. To integrate the needed amount of catalyst, high porous substrate materials have been developed. A drawback of the high porosity levels of 60% and higher is a significant reduction in mechanical strength. The aim of this work is to provide a new solution based on a high porous SiC material which is treated by a dual layer coating. The first layer is a nanoparticle coating which enhances the mechanical strength of the substrate. It can also be used to improve the catalytic performance and to finally decrease the loading of the second coating layer which is the active catalyst for selective catalytic reduction (SCR) of NO_x with ammonia.

Three different types of catalysts have been investigated as the second layer: a Fe-β-zeolite, a mixed metal oxide based on ceria and zirconia and a composition based on titania and vanadia. The impact on the pore structure and the resulting back pressure was investigated as well as the SCR functionality. The results demonstrate that the combination of the initial nanoparticle layer with the different catalyst layers has led to high SCR efficiencies at low catalyst loadings.

Engine bench tests on filters in the size of 5.66"×8" have been performed to verify the high particle number (PN) filtration efficiency which is required for Euro 6/VI applications and the NO_x reduction efficiency by using a diesel oxidation catalyst (DOC) for adjusting the NO₂/NO_x ratio. The results demonstrate that a new type of a diesel particle filter (DPF) has been developed, in which various types of SCR catalysts can be integrated. This new filter with integrated SCR functionality can be used in the design of exhaust systems with reduced volume, weight and costs, which still meet the Euro 6/VI requirements in respect to NO_x and PN reduction for petrol and diesel engines.

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INTRODUCTION

Wall flow DPFs are the established solutions for particle number reduction up to 99.99% to comply with EURO VI regulations. To meet the NO_x emission levels SCR is the established technology. Reduction of overall system costs, space and fuel consumption are the main driving factors for future development. First investigations have shown that the integration of the SCR catalyst into the DPF is an effective way to fulfill these requirements in respect to space and costs. Naseri *et al.* [1] investigated a SCR coated DPF combined with a flow through SCR and found an improved DeNO_x functionality as well as an optimized passive regeneration at 400°C at a reduced system packaging volume. Tan *et al.* [2]

demonstrated the reduction of the total exhaust after treatment catalyst packaging by combination of a DPF with SCR functionality combined with a conventional flow through SCR catalyst which led to a reduction of the SCR volume by 55%. They found that an equivalent DPF passive regeneration can be achieved at temperature levels 20°C - 30°C higher compared to catalyzed DPF solutions. In both papers the regeneration strategy is passive regeneration and in either cases the needed temperature for that is 380°C - 400°C which is relatively high. The used DPF substrate was a cordierite at 59% and 65% porosity. These systems are very sensitive to regeneration and any overload can cause severe damage. According to Tan *et al.* [2] in a 600-to-idle test the coated

cordierite at 65% porosity already reached a peak temperature of more than 1000°C at a soot load of 5.3 g/l, which caused cracks in the filter. For the 59% porosity cordierite these temperatures are reached at 6.8g/l. However, the used Cu-zeolite SCR catalyst was already damaged at 900°C. These results [2] indicate that SCR on DPF solutions based on cordierite have a very restricted soot load level. To have a better protection of the catalyst itself, silicon carbide can be chosen as the substrate material. This material has a higher density and heat capacity than cordierite. Examples are given by Kawakami et al. [3] and Nakamura et al. [4]. They both report on high porous SiC structures with an additional coating on the inlet side. Another high porous SiC filter material was presented by Ogyu et al. [5] where an enhanced stability of a porous SiC at a porosity level of more than 60% was achieved by high temperature oxidation resulting in a thin SiO₂ film. All these SiC based systems will be used for future passenger car SCR on DPF solutions, where a robust high porosity DPF is needed. But they are also potential candidates for robust solutions in the HDD and off-road sector.

Beside the discussion of the temperature resistance of high porous substrate materials it has to be borne in mind that the integrated SCR catalyst also has to be resistant against elevated temperatures. It is commonly known that for vanadia based SCR systems temperatures should not exceed 650°C. Maunula et al. [6] have recently shown that the usage of TiO₂-WO₃ stabilized raw materials in vanadia systems lead to an increase of the temperature stability up to 750°C. The above mentioned zeolites show a reduced SCR performance after ageing at temperatures higher than 750°C. Rohart et al. [7] and Marcotte et al. [8] describe a new kind of SCR active catalysts which can withstand 750°C without losing their performance and are phase stable up to 1000°C. These catalyst materials are based on a mixture of cerium and zirconium oxide enhanced by dopants and are also known as "mixed metal oxides". Stakheev et al. [9] even use these mixed metal oxides to reduce the amount and simultaneously enhance the SCR activity of a Fe- β -zeolite.

A high porous SiC based on a reaction forming or also called silicization process is already described by Wolff et al. [10]. Based on that technology a new type of a high porosity SiC was developed, which has an improved capability for SCR coatings. In the following it is described, how the mechanical strength of the fragile high porosity material is enhanced by a first coating layer based on a colloidal sol and how this first coating can be used to optimize the efficiency of the second coating layer based on a SCR catalyst.

THE HIGH POROUS SiC SUBSTRATE

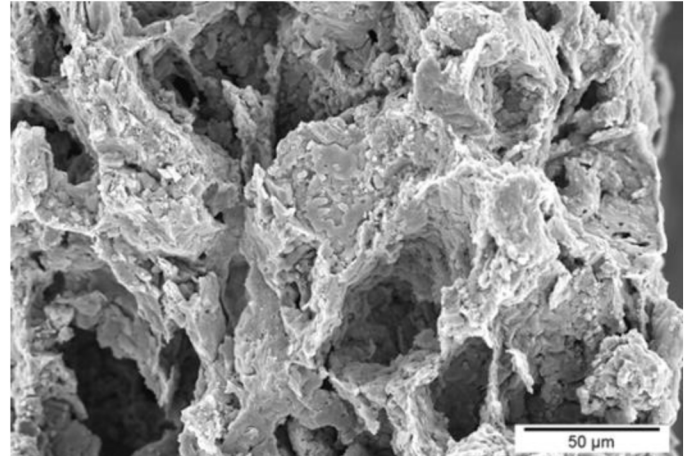


Figure 1. β -SiC created at 1400°C from silicon, carbon and aluminum according to Wolff et al. [10].

The substrate used for all samples in this work was a high porous SiC at a porosity level of 65% and a mean pore diameter of 18 μ m - 20 μ m. In contrast to most of the SiC materials on the market this type is made by a reaction forming process followed by a pore opening process. The reaction forming process is based on earlier work [10]. On basis of the raw materials graphite, metallic silicon and metallic aluminum a porous β -SiC structure is created at moderate temperatures between 1350°C and 1450°C. In a subsequent heat treatment in a temperature range of 1700°C - 1980°C the structure and pore size can be modified [11]. The changes in morphology during this high temperature step can be observed in Figure 1 and Figure 2.

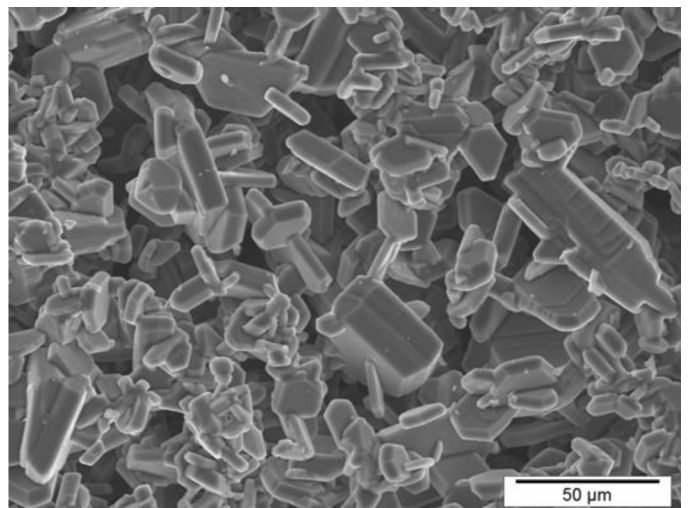


Figure 2. α -SiC after temperature treatment due to [11] of a β -SiC structure shown in Figure 1.

The final high porous SiC structure is built up by plate-like hexagonal SiC crystals. With this production method it is possible to generate high porous structures at moderate pore sizes. The pore size combined with the skeleton built up by the plate-like hexagonal crystals allows creating highly porous filter substrates.

The typical material properties of the here shown SiC substrate are listed for a 65%-type version in [Table 1](#).

Table 1. Material data for a high porous SiC with 65% porosity, 20µm pore diameter in 200cps/400µm honeycomb.

CTE (RT – 800°C), 1/K	4.7
Therm. heat cond. 400°C, W/mK	2.2
Spec. heat capacity 400°C, J/gK	1.032
Bending strength, MPa	2.8
Maximum operating temperature, °C	1400

THE TWO COATING LAYERS

First Coating Layer for Improvement of Strength

A consequence of the high porosity is a reduction in mechanical strength. Especially the type with 65% porosity is quite fragile; a 200cps honeycomb with 400µm wall thickness has a bending strength (4-point-bending due to ASTM C-1674) of 2.8 MPa. To enhance the strength an initial coating layer was applied to the SiC substrate. The initial coating layer was given in form of a colloidal silica sol. The sol or rather the nanoparticles fill up mainly the very fine and small intermediate spaces between the crystals, which build up the structure of the porous network. This leads to an enforcement of the connections and bridges between the crystals and as a result of that to an increase in mechanical strength. The crystals are covered with a very thin layer of the sol particles resulting in a smoothing of the edges of the crystals. Due to the fact that mainly the intermediate spaces in the pore walls are filled, the accessible porosity is reduced but not the main pore diameter. The impact of the silica sol layer/coating on porosity, pore size and corresponding back pressure data is shown in [Figure 3](#).

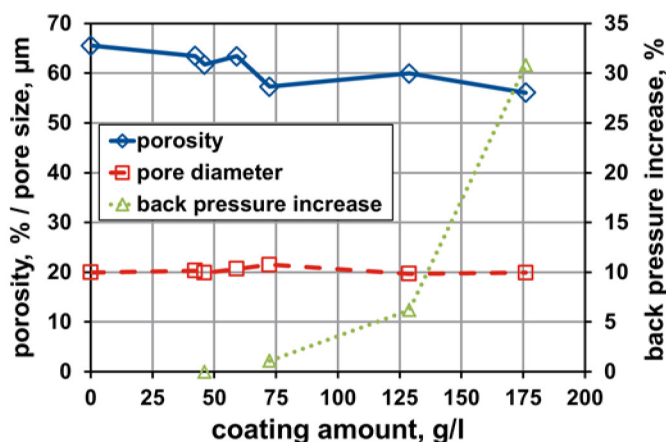


Figure 3. Impact on porosity, mean pore diameter and back pressure by coating with different amounts of colloidal silica sol.

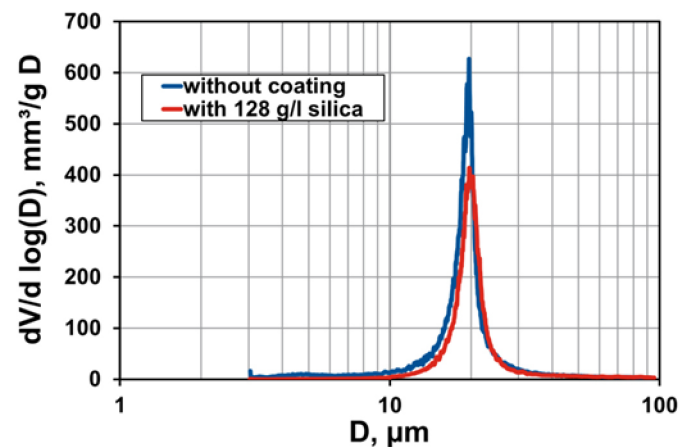


Figure 4. Pore size distribution of a SiC with 65% porosity and 20µm mean pore diameter with and without silica sol coating layer.

The decrease of the porosity from initial 65% down to 57% at almost 180g/l loading can be observed. The mean pore diameter is kept constant. This characteristic of the sol coating can be discovered by comparison of the pore size distribution measured by mercury intrusion porosimetry for the uncoated and coated structure. [Figure 4](#) shows such a comparison. The very small pores are filled up with the coating and the overall accessible porosity is decreasing, but the median pore diameter remains the same.

The mechanical strength was tested with the 4-point-bending test method. The results are shown in [Figure 5](#). The value of 2.8MPa for the uncoated structure could be increased to 3.4MPa with a coating of about 46g/l. Due to this effect, the initial coating for achieving higher mechanical strength can be understood as an impregnation layer, which fills up small dead end pores up to a diameter of about 5µm resulting in a smoothing of the pore surface.

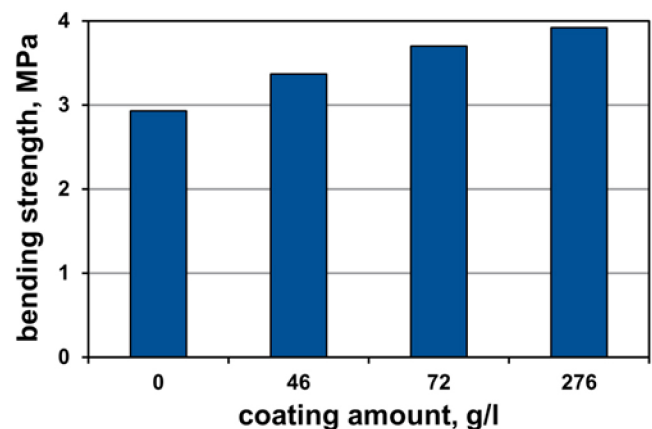


Figure 5. Bending strength vs. amount of coated silica on SiC substrates with 65% porosity and 20µm pore size (200cps/400µm).

Table 2. Characteristic features of different SCR catalysts.

	Vanadia-based (V_2O_5/WO_3-TiO_2)	Cu-Zeolite (Cu-ZSM-5)	Fe-Zeolite (Fe- β)	Mixed metal oxide (CeO ₂ -ZrO ₂ based)
Function of every single compound	V ₂ O ₅ : SCR active center WO ₃ : promoter TiO ₂ : support	Cu: NO oxidation to NO ₂ ZSM-5: host, SCR reaction, NH ₃ storage	Fe: NO oxidation to NO ₂ Beta: host, SCR reaction, NH ₃ storage	CeO ₂ : SCR active center, O ₂ storage ZrO ₂ : thermal stabilizer, NH ₃ storage
SCR activity	High (dependent on V ₂ O ₅ content, best: ~ 3 wt%)	High at low temperatures steadily decreasing beyond 350°C	High (at high temperatures up to 600°C, above NH ₃ over-consumption) Low (< 300°C)	High (variable temperature window dependent on Ce/Zr ratio, dopants, surface area + water content)
SCR temperature interval	T ₅₀ : 200°C ≥ 90%: 300°C – 500°C	T ₅₀ : 180°C ≥ 90%: 250°C – 400°C	T ₅₀ : 300°C ≥ 90%: 400°C – 650°C	T ₅₀ : ~ 250°C or lower ≥ 90%: ~300°C – 500/550°C dependent on Ce/Zr ratio + dopants
NH ₃ storage	Low	High	High	Medium
NH ₃ slip	Yes (dependent on dosing)	Only if overdosed ($\alpha > 1$), though ~10% of NH ₃ consumed in oxidation to N ₂	Only if overdosed ($\alpha > 1$), though ~10% of NH ₃ consumed in oxidation to N ₂	Yes (dependent on dosing, lower NH ₃ storage than zeolites)
Selectivity	Good up to 450°C	Good	High (up to high temperatures)	High
N ₂ O formation	Increasing formation at >400°C (at 10 ppm NH ₃ slip)	High formation tendency even at low temperatures	No formation Reduces N ₂ O to N ₂ above 400°C	Low formation tendency
Toxicity	V ₂ O ₅ volatility (>690°C)	Concerns due to CuSO ₄ creation	No	No/low

For the further development a coating amount of the first layer was chosen which is high enough to create a significant improvement in mechanical strength but which is on the other side still low enough to keep the back pressure increase at a small level. Combining the results shown in [Figure 3](#) and [Figure 5](#) the loading should be in the range of 50g/l to 75g/l.

Even though not explicitly tested, it can be assumed that the CTE does not change significantly by this coating. The thermal expansion and conductivity is mainly given by the SiC lattice structure.

Second Coating Layer for SCR Functionality

In the following it is described, how the initial impregnation layer will be combined with a second layer of a catalytic functional material such as SCR active materials.

As SCR active coatings for exhaust after treatment there are three different kinds of catalyst materials in commercial use. These are vanadia, zeolite and mixed metal oxide based systems. Yet they all exhibit slightly different properties and are therefore not fully interchangeable but each of them can be the optimal choice for different applications.

Vanadia based SCR catalysts are usually used to keep costs as low as possible. However this kind of catalyst has to be treated carefully. When exhaust gas temperatures exceed 650°C the SCR activity is irreversibly decreasing. The reasons for this are the phase transformation of anatase to rutile as well as the evaporation of vanadia. Apart from that vanadia vapour is known to be highly toxic.

The two most common zeolites used for SCR are the Cu-ZSM-5 and the Fe- β . Cu-ZSM-5 is known to have an excellent low temperature performance, but is very likely to produce N₂O, whereas Fe- β has an extraordinarily high-temperature SCR activity even beyond 500°C. However they are both highly expensive compared to vanadia based systems, but are thermally more stable up to higher temperatures (> 750°C).

Ceria-zirconia based mixed metal oxides are supposed to be thermally stable up to 1000°C, but this strongly depends on the total composition and the kind of dopants used. They are usually highly SCR active over a broad temperature range as long as the water content is kept very low. Moreover these catalysts might exhibit some soot and CO oxidation properties [9]. [Table 2](#) gives an overview on the different types of SCR catalysts and some of their characteristic features.